CF_3Br and Other Suppressants: Differences in Effects on Flame Structure

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Background

Halon 1301 (CF_3Br) production banned in developed countries since 1994, worldwide by 2005.

Generally considered as a catalytic scavenger, due to H + H => H_2 cycle involving bromine atom. Responsible for slightly more than half of total suppression effect.

Combustion chemistry of CF_3 moiety and high molar heat capacity contribute remainder of suppression.

Many experimental and modeling studies have investigated CF_3Br as a baseline for:

- Determining effectiveness of alternatives
- Inferring behavior of catalytic suppressants in general

Classes of Suppression Agents

- Thermal (N_2, CF_4, H_2O, CO_2)
  End products or inert in flame. Add heat capacity, dilute reactants
- Catalytic chemical (iron, sodium, potassium)
  One atom of active element recombines several flame radicals usually to stable products:
  $H, O, OH \longrightarrow H_2, O_2, H_2O$
- Noncatalytic chemical (hydrofluorocarbons)
  Chemistry of agent slows overall kinetics and reduces radical pool in flame, but no catalytic cycle

Catalytic agents are usually the most efficient

How should CF_3Br be classified?

CF_3Br is a catalytic agent because of bromine

Bromine chemistry not the only effect

- CF_3 moiety makes a significant contribution

Br is not a very efficient scavenger

- Other elements (potassium, phosphorus, iron) are more than ten times better (Tsang and Babushok, *C&F*, 2001)

Questions explored in this study

How do changes in premixed flame structure induced by CF_3Br inhibition compare to effects of other agents: catalytic chemical, non-catalytic chemical, inert?

Is CF_3Br "typical" of efficient fire suppressants in general?

Will all promising replacements for CF_3Br show similar behavior?

Is commonality of properties with CF_3Br a useful guide in the search for alternatives?

Computational Details

This study: computational investigations of various categories of inhibitors on structure and burning velocity of premixed, atmospheric pressure stoichiometric methane/air flames.

- PREMIX
- Gri-Mech 2.11(no nitrogen chemistry) for hydrocarbon kinetics

  inert agents: N_2, CF_4 (assume no fluorine chemistry)
- Various submechanisms for other types of agents:

  fluorocarbon: CF_3CHFCF_3, CF_3CH_2F, CF_3Br

  catalytic: $Fe(CO)_5$, NaOH

How does Inhibition vary with Agent Concentration?

For many inhibitors, burning velocity has an exponential dependence on inhibitor concentration:

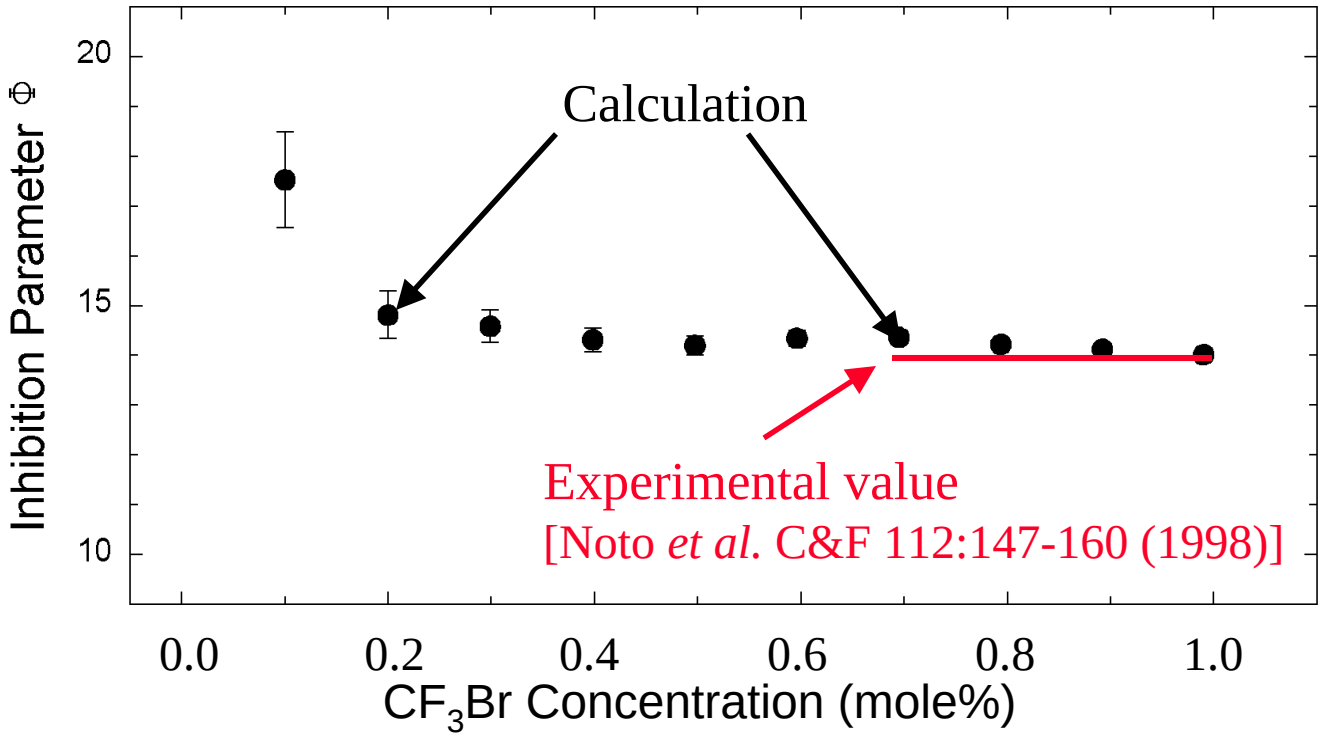
$U_i = U_o \exp(-\Phi X_i / X_{O2})$

X_i= mole fraction of inhibitor
U_i= inhibited burning velocity

$\Phi = \ln(U_o/U_i)(X_{O2}/X_i)$
"inhibition parameter" [Noto *et al.* C&F 112:147-160 (1998)]

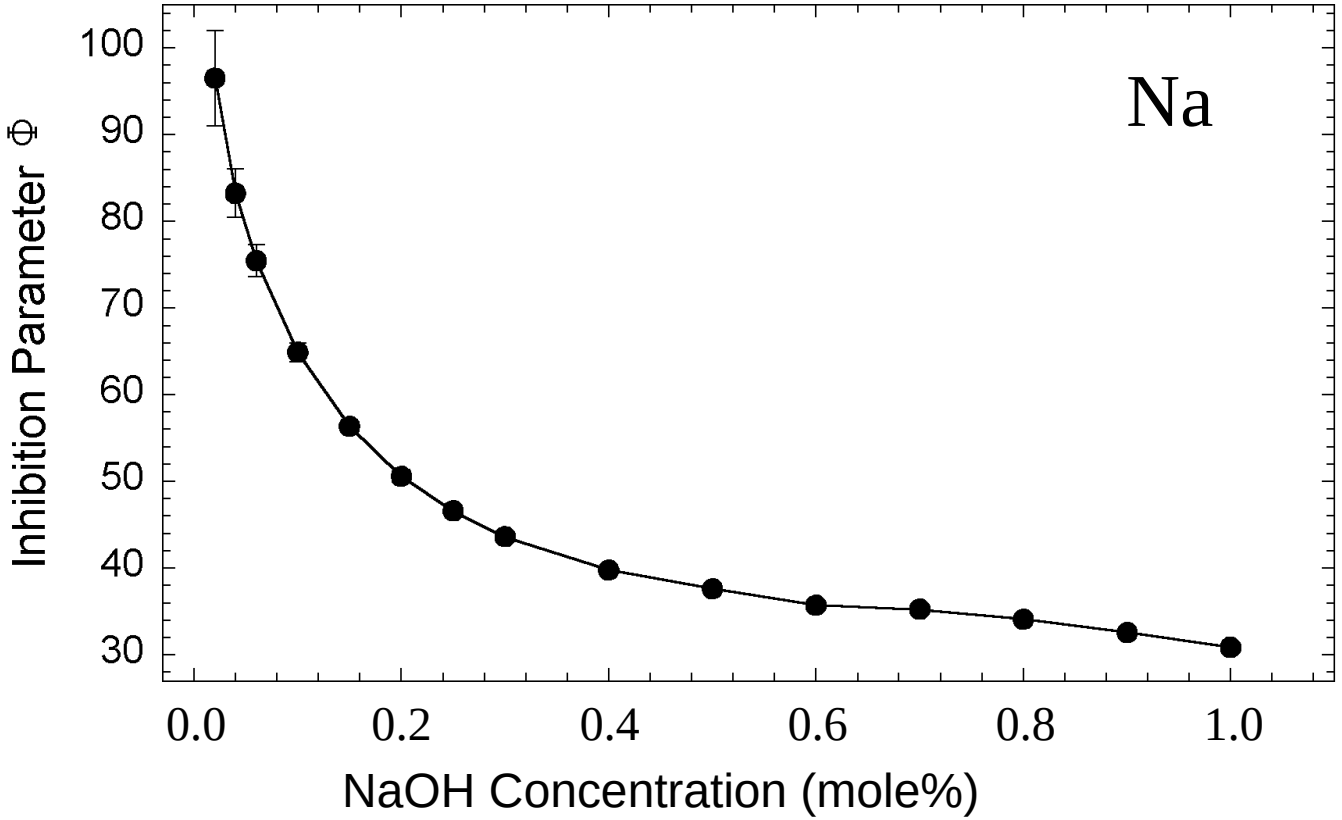
For many inhibitors including N_2, several fluorocarbons (both inert and reactive), and CF_3Br, Φ is independent of agent concentration--exponential law holds.

Exponential Law Holds for CF_3Br



Φ is constant from 0.2% to 1% mole fraction CF_3Br. Flame speed drops by more than a factor of two over this range.

But, Exponential Law does not Always Hold



Most catalytic scavengers, including sodium and iron, do *not* follow the exponential dependence due to saturation effects.

Why doesn't CF_3Br show saturation?

- Bromine not a very good chemical scavenger
- A significant proportion of chemical effects come from noncatalytic effects of fluorine atoms.
- Bromine catalytic pathway includes a second order reaction:

$Br+Br \Rightarrow Br_2$; $H+Br_2 \Rightarrow HBr+Br$; $H+HBr \Rightarrow H_2+Br$

Two consequences of second order kinetics:

- Scavenging becomes more efficient at higher concentrations—counterbalances saturation.
- Need high bromine concentration for this reaction to become significant!

Synergism between CF_3Br and Physical Agents

Saso et al. (C&F 1999) demonstrated synergism in CF_3Br/inert mixtures.

Conclusion: Synergism is primarily due to temperature dependence of Br kinetics. Saturation doesn't play an important role.

- Lower temperature makes Br cycle more efficient.
- Weak Br-Br bond consistent with this observation.
- Phosphorus compounds may have a similar temperature dependence (more efficient inhibition at lower temperature [MacDonald *et al.*, C&F 2001])

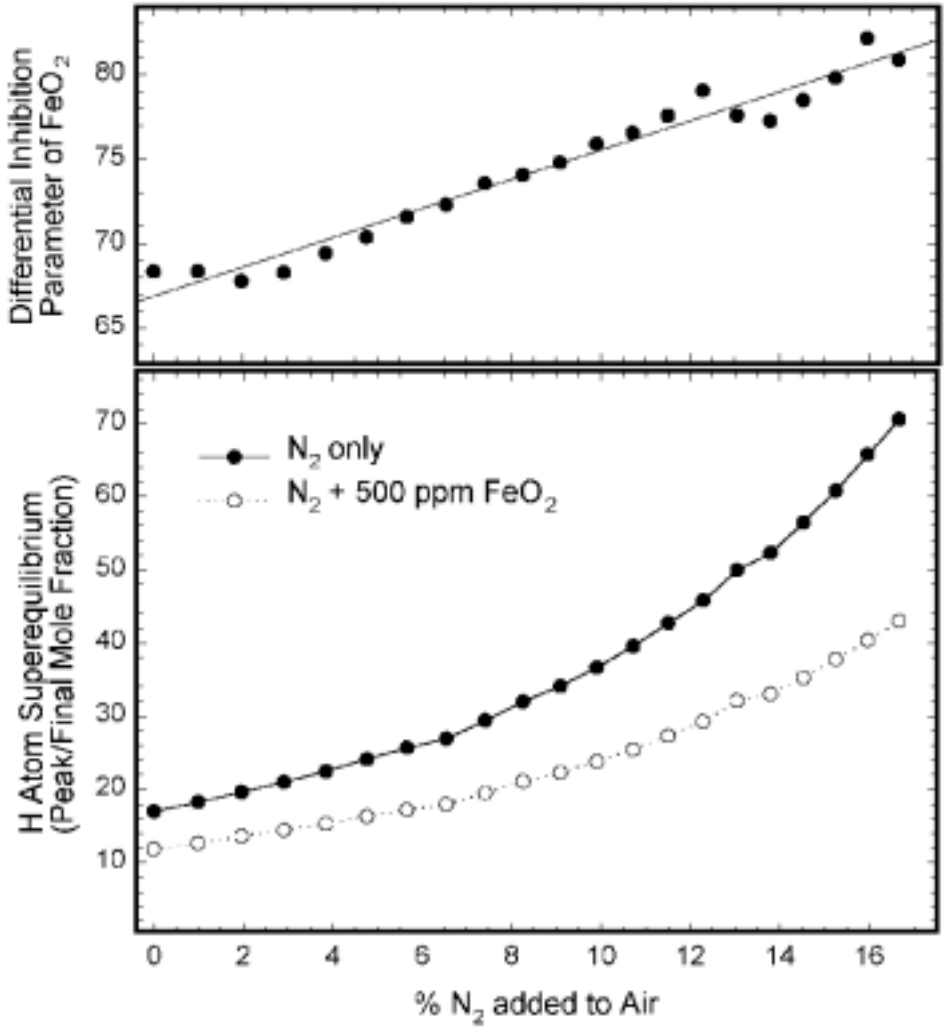
Synergism between Iron and Physical Agents

Mixture of iron and nitrogen: inhibition parameter of Fe increases as N_2 is added

No temperature dependence in kinetics of this catalytic cycle

Physical agent creates more radical superequilibrium for the catalytic agent to exploit

Temperature dependence of kinetics not required for synergism



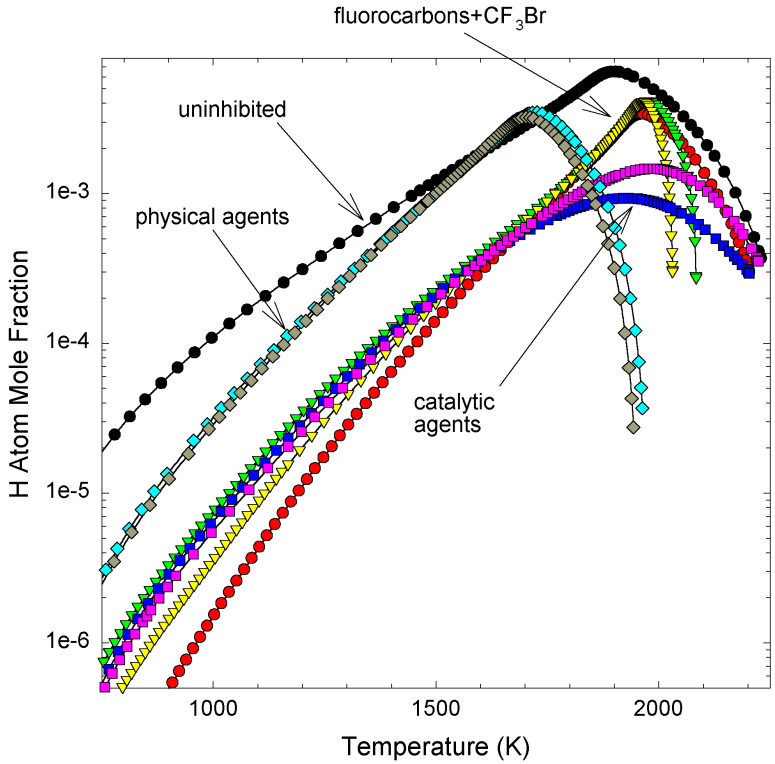
Antagonism Between Catalytic Inhibitors Used in Combination

Agent	Flame Speed (cm/s)	Inhibition Parameter Φ
none	39.6	---
0.2% $(NaOH)_2$	17	40.1
0.1% FeO_2	29.5	56.1
0.2%$(NaOH)_2$ + 0.1% FeO_2	14.9	32.4(Na) 24.9(Fe)

In this model, Na only reacts with H and OH, Fe only reacts with O. Nevertheless, they reduce each other's effectiveness.

Effect of Different Agents on Flame Structure

For most inhibited flames, burning velocity correlates with peak H atom concentration and adiabatic flame temperature.
Exceptions: CF_3Br, HBr, hydrofluorocarbons.



- CF_3Br reduces H atom concentration early in flame (like fluorocarbons)
- Other catalytic agents reduce [H] throughout flame
- Inerts reduce final temperature, but leave [H] relatively unchanged at a fixed temperature.

Peak H atom concentration and flame speed

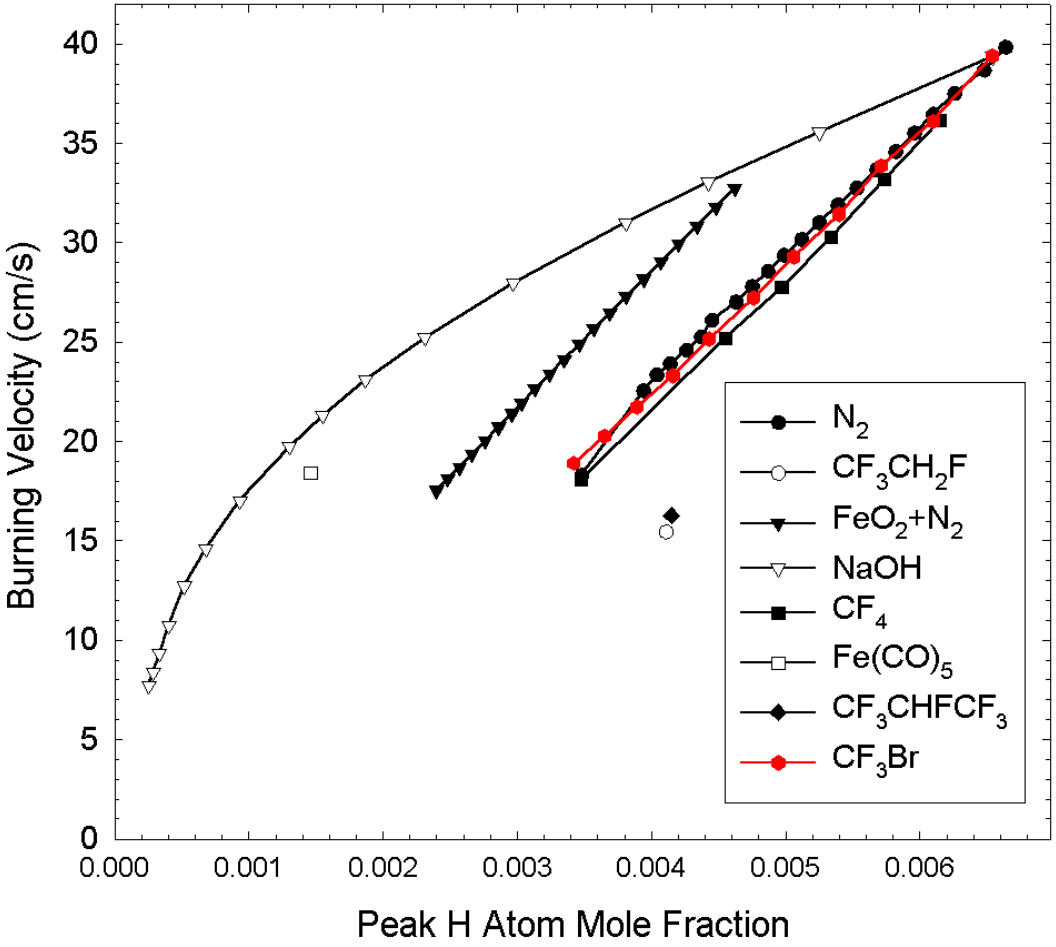
Padley and Sugden: $H_2/O_2/N_2$ burning velocity ∝ partial pressure of atomic hydrogen in the reaction zone.

Kim, Kwon, Faeth: proportionality holds for hydrogen flames inhibited by CF_3Br.

Relationship not universal:

- Catalysts reduce H atom more than burning velocity
- Fluorocarbons reduce burning velocity more than H atom

CF_3Br: cancellation of two effects?



Idiosyncrasies of CF_3Br

- An important reaction in scavenging pathway has second order kinetics in agent concentration: Br+Br+M => Br_2+M
- No significant saturation effects--unlike most other catalytic fire suppressants.
- Synergism in CF_3Br mixtures due primarily to explicit temperature dependence of kinetics, not change in radical superequilibrium.
- CF_3Br does not deplete atomic H concentration uniformly throughout flame, only early in flame zone.

Conclusions

There are good reasons for choosing CF_3Br as a *performance* benchmark for alternative suppressants, given the fire protection community's experience with this agent.

Many of the details of CF_3Br's kinetics and behavior are idiosyncratic: they are not shared by other catalytic suppressants.

Several issues for alternative agents, e.g. vaporization rate for condensed phase agents, do not come into play for CF_3Br.